Acid catalysed rearrangements of 1-hydroxy-2,3,4,4a-tetrahydro-9*H*-xanthen-9-ones: synthesis and cycloaddition reactions of 3,4-dihydro-9*H*-xanthen-9-ones

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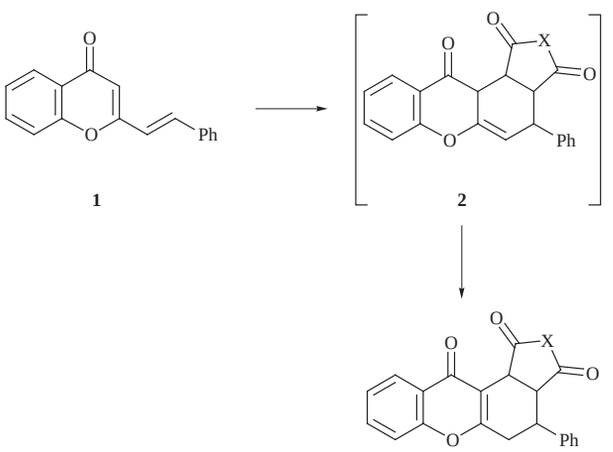
The acid catalysed rearrangement of 1-hydroxy-2,3,4,4a-tetrahydro-9*H*-xanthen-9-ones can give 1-alkoxy- or 1-alkylidene-1,2,3,4-tetrahydro-9*H*-xanthen-9-ones and/or 3,4-dihydro-9*H*-xanthen-9-ones depending on the conditions employed. The last compounds undergo facile Diels–Alder cycloaddition reactions.

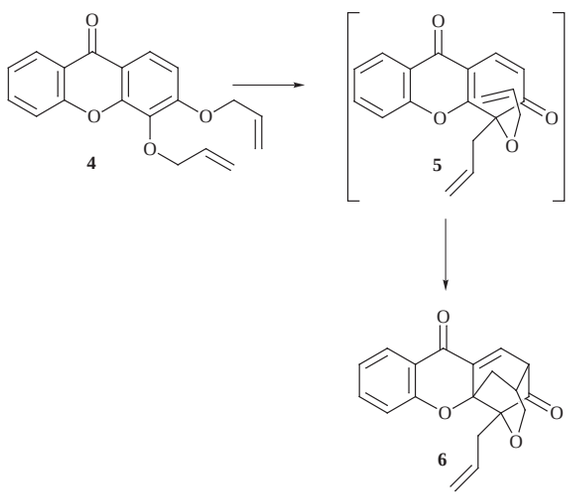
Diels–Alder reactions of 2-styrylchromones leading to reduced xanthone derivatives have been known since 1954,[1] when the tetrahydroxanthone **2** (X = O) was obtained from the reaction of 2-styrylchromone **1** with maleic anhydride. In a similar manner, **1** reacts with *N*-methylmaleimide to give xanthone **2** (X = NMe).[2] However, Letcher and Yue have recently revised the



structures of these cycloadducts from the chromanone-based tetracycle **2** to the isomeric chromone system **3**.[3] Cycloadditions of 2-styrylchromones have also been carried out with dibenzoylethylenes[4] and 1,4-benzoquinones[5] to give the corresponding tetrahydroxanthones, though the proposed structures may also need revision.

During an investigation into the construction of the morellin series of natural products, Quillinan and Scheinmann[6] demonstrated that 3,4-diallyloxyxanthone **4** was converted into the bicyclo[2.2.2]octenone **6** on heating. An initial Claisen rearrangement involving a shift of the 3-allyl group to the 4-position afforded the 3,4-dihydroxanthone **5** which underwent an intramolecular [4 + 2] cycloaddition. Some 3-substituted 3,4-dihydroxanthones have been reported by Fry.[7]. Thus, treatment of xanthone with lithium 4,4′-(di-*tert*-butyl)biphenyl generated a dianion which reacted with benzylic and *tert*-butyl halides to give 3-alkyl-3,4-dihydroxanthen-9-ones. However, the corresponding reaction with primary alkyl halides led solely to the 9-alkylxanthen-9-ol derivative.

We have previously shown that 3-hydroxymethylidenechroman-4-ones undergo an acid catalysed rearrangement to give 3-alkenylchromones.[8] We now report the application of

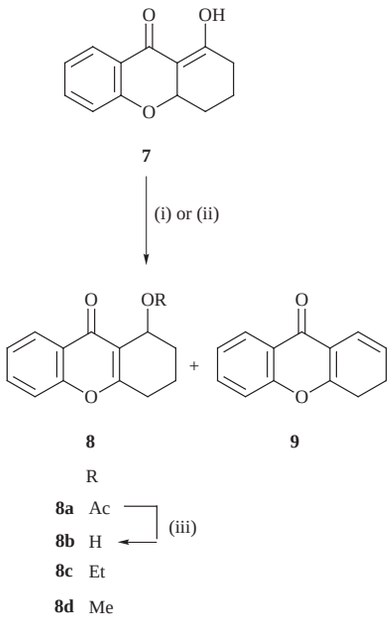


this rearrangement to 1-hydroxy-2,3,4,4a-tetrahydroxanthones[9] which provides a novel route to 3,4-dihydroxanthones. The use of these compounds as Diels–Alder dienes is also described.

Discussion

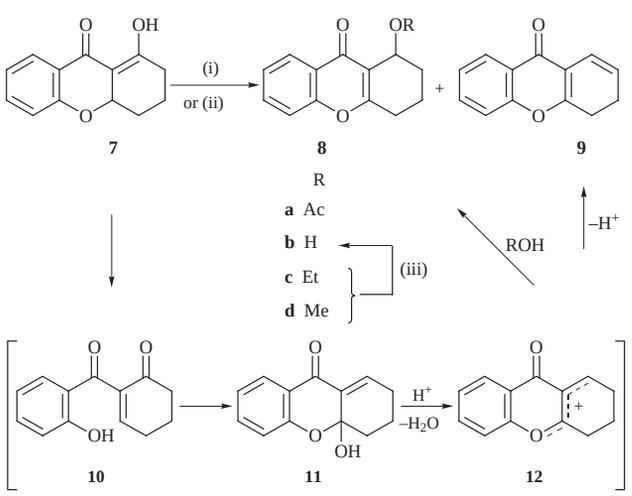
Reaction of the xanthone **7** with toluene-4-sulfonic acid in pyridine, the preferred conditions for alkenylchromone formation,[8] gave xanthone-9-one exclusively and in excellent yield (Scheme 1). Conducting this reaction in degassed pyridine under an inert atmosphere still gave xanthen-9-one in high yield; the nature of the oxidation step in this reaction remains unclear. The use of alternative rearrangement conditions, namely 1,4-diazabicyclo[2.2.2]octane (DABCO) in acetic acid,[8] gave two products which were separated by column chromatography. The major product was the tetrahydroxanthone **8a** (64%) whilst the minor isolated product was the dihydroxanthone **9**. The yield of 1-acetoxytetrahydroxanthone **8a** was increased to 80% by replacing the amine base with sodium acetate and under these conditions no **9** was observed (Scheme 1). Mild acidic hydrolysis of **8a** gave 1-hydroxytetrahydroxanthone **8b** in excellent yield, identical with that reported in the literature.[10] It is known that compound **8b** has antianaphylactic properties and the present procedure represents a greatly improved route to this compound, since the existing method is both laborious and low yielding.

Treatment of diketone **7** with toluene-4-sulfonic acid in absolute ethanol gave an excellent yield of the ether **8c** after pro-



Scheme 1 *Reagents and conditions*: (i) DABCO, AcOH, Δ; (ii) NaOAc, AcOH, Δ; (iii) HCl, AcOH

longed reflux. No other products were observed under these conditions. The use of aqueous ethanol as solvent resulted in a decreased yield of **8c**, but **8b** was also formed. This change was enhanced as the amount of water was increased and only 33% of **8c** was formed together with 46% of the hydroxytetrahydroxanthone **8b** when a 2:3 ethanol–water mixture was used. When methanol replaced ethanol, the 1-methoxy analogue **8d** was obtained in modest yield (35%), the balance of material being unreacted **7**. The mechanism of these reactions probably involves the acid catalysed ring scission of **7** leading to the ketone **10**, followed by bond rotation and closure to the hemiacetal **11**. Subsequent loss of water gives carbocation **12** which can either be trapped by solvent to yield **8** or deprotonated to **9** (Scheme 2). The interception of chromanone carbocations by



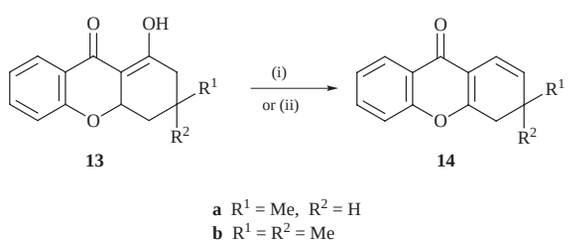
Scheme 2 *Reagents and conditions*: (i) DABCO, AcOH, Δ; (ii) TsOH, ROH, Δ; (iii) BBr_3, CH_2Cl_2, −40 to −10 °C, N_2

polar solvents has been reported previously by Eiden and Luft during their studies into the acid catalysed dehydration of chromanone hemiacetals.[11] The anomalous products observed by us during alkenylchromone formation result from a similar pathway.[8] The susceptibility of 3-acylchromanones to undergo self-condensation *via* carbocation intermediates has been noted by Dean.[12]

Treatment of ethers **8c** and **8d** with boron tribromide in dichloromethane[13] resulted in dealkylation with the formation of **8b** in high yield (Scheme 2).

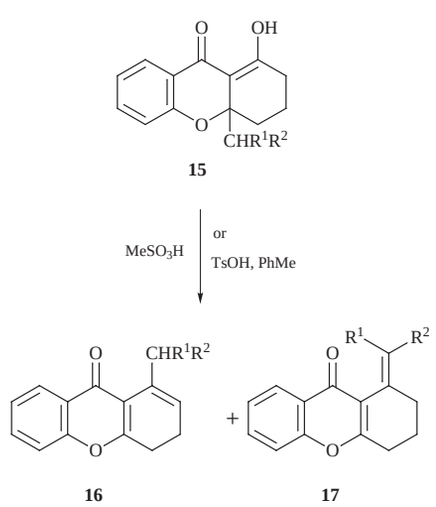
The inefficiency of the acid catalysed conversion of diketone **7** to the diene **9** is largely a consequence of the polar solvent intercepting the carbocation **12**, advocating the use of an inert solvent for the rearrangement. Toluene containing *p*-TsOH was found to be an ideal choice and **7** was converted to **9** in almost quantitative yield. It was also found that diketone **7** was smoothly converted to **9** in excellent yield using neat methanesulfonic acid at room temperature. Indeed, under these latter conditions chromatographic isolation of the product was unnecessary. The efficacy of methanesulfonic acid for a variety of dehydrations and cyclodehydrations has been noted.[14]

Deprotonation of the cation **12** in Scheme 2 can lead to two different alkenes because the substrate possesses alternative β-hydrogen atoms. This aspect of the rearrangement was investigated by studying the behaviour of several 3- and 4a-substituted xanthones **13** and **15**. The rearrangement of the 3-substituted derivatives **13a** and **13b** proceeded smoothly to yield the 3,4-dihydroxanthones **14a** and **14b** respectively in nearly quantitative yields (Scheme 3). The rearrangement of the



Scheme 3 *Reagents and conditions*: (i) TsOH, PhMe, Δ; (ii) $MeSO_3H$, 25 °C

Table 1



Compound	R^1	R^2	Ratio[a] **16**:**17**	Yield (%)
a	H	H	8:2	99
b	H	Me	1:5	97
c	H	Pr^n	3:7	99
d	Me	Et	1:0	100
e	H	4-Methylphenyl	0:1	92

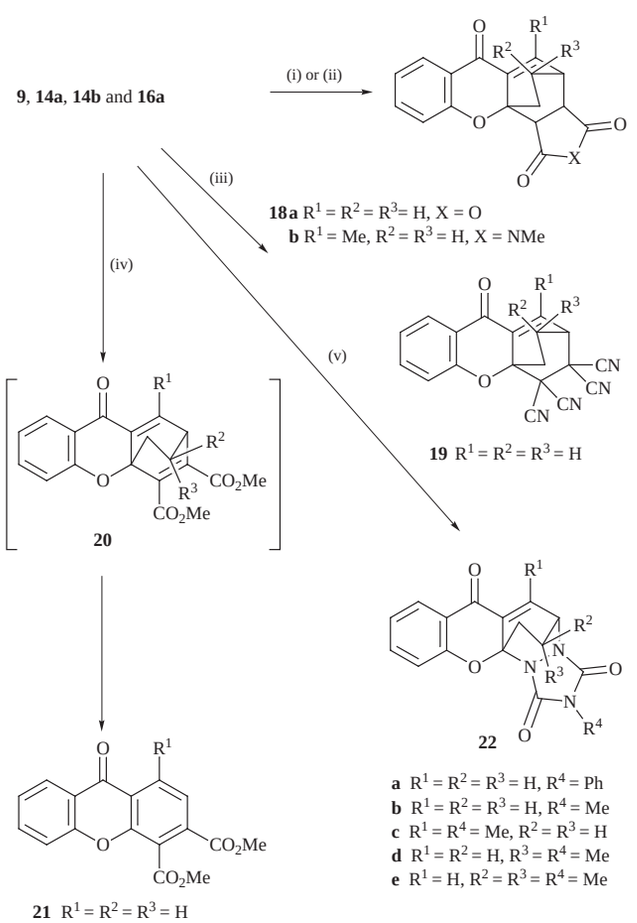
[a] Ratio of products **16**:**17** determined from ^1H NMR spectra.

4a-methylxanthenedione **15a** led to a *ca.* 4:1 mixture of the corresponding 1-methylxanthone **16a** and the exocyclic olefin **17a** (Table 1) from which only the former could be obtained in a pure state. The latter displayed ^1H NMR signals at δ 5.28 and 6.65 (J 2.2 Hz) which corresponded to the *exo*-methylene

function, with the low field doublet associated with the proton *syn* to the carbonyl group.

Other 4a-substituted xanthones **15** also rearranged in excellent yields on treatment with toluene-4-sulfonic acid in toluene or with methanesulfonic acid. The structure of the products varied with nature of the substituent and the rearrangement conditions as detailed in the experimental section. The ethyl **15b** and *n*-butyl **15c** derivatives behaved like the methyl compound **15a** and gave mixtures of the *endo*- and *exo*-cyclic dienes **16** and **17**, which have the stereochemistries shown in Table 1. Other examples underwent regiospecific eliminations. Thus, the *sec*-butyl compound **15d** gave only the *endo*-product **16d**, whilst the 4-methylbenzyl derivative **15e** gave the exocyclic diene **17e** exclusively. Presumably the stability arising from the extended conjugation in **17e** outweighs the steric advantages associated with **16e**. Molecular models indicate severe steric hindrance in **17e** when the alkenic proton is *anti* to the carbonyl function and the structure given in Table 1 is assumed to be correct. Some support for this view is the low-field resonance for the benzylidene proton which appears at δ 8.31.

The dienes **9** and **16** can be considered of even greater synthetic potential in cycloaddition reactions than 2-styrylchromones **1** because the diene portion is locked into the *cis* configuration and some applications are shown in Scheme 4. Reaction of **9** and **16a** with maleic anhydride and *N*-



Scheme 4 *Reagents and conditions*: (i) maleic anhydride, PhMe, Δ; (ii) *N*-methylmaleimide, PhMe, Δ; (iii) TCNE, THF, 25 °C; (iv) DMAD, PhBr, Δ; (v) MTAD or PTAD, CH_2Cl_2, 25 °C

methylmaleimide in refluxing toluene gave the adducts **18a** and **18b** respectively and even the moderate yields obtained represent an improvement over the corresponding reactions with the simpler styrylchromones. Characterisation of these novel xanthones was achieved by inspection of their ^{1}H NMR spectra. Signals for H-3a and H-11b in **18a** are present at 3.66 and 3.78 ppm as a double doublet and doublet, respectively. Both protons are mutually coupled ($J_{3a,11b}$ = 8.6 Hz) and H-3a also displays coupling to the bridgehead H-4 ($J_{3a,4}$ = 3.1 Hz). The most likely mode of addition is *endo* by comparison of coupling constants with those for the adducts of cyclohexa-1,3-dienes with maleic anhydride.[15] The integrity of the chromanone nucleus is confirmed from signals for H-7 at 7.82 and H-5 at 7.38 ppm, respectively. The latter signal is coupled to H-4 ($J_{5,4}$ = 6.3 Hz). A similar spectrum was observed for **18b**.

Tetracyanoethylene (TCNE) is one of the most reactive Diels–Alder dienophiles.[16] Reaction of **9** with this reagent in tetrahydrofuran at room temperature gave the adduct **19** in moderate yield. The infrared spectrum of **19** showed a chromanone carbonyl stretch at 1676 cm^{-1}, although remarkably no nitrile stretching bands were observed. However, the constitution of this compound was supported by elemental analysis. The ^{1}H NMR spectrum confirmed the benzopyranone nucleus for **19** by a signal for H-1 at 7.68 ppm and for H-8 at 8.04 ppm.

Dimethyl acetylenedicarboxylate (DMAD) reacts with cyclohexadienes to give arene dicarboxylic esters as a result of an initial [4 + 2] cycloaddition and a subsequent retro Diels–Alder elimination of the alkyl bridge.[17] Reaction of DMAD with either **9** or **14b** in boiling bromobenzene gave a good yield of dimethyl 9-oxoxanthene-3,4-dicarboxylate **21** by way of the intermediate adduct **20** which decomposed *via* thermal extrusion of ethylene and isobutene respectively. The xanthone **21** was characterised by its infrared and ^{1}H NMR spectra. The ester carbonyl absorptions were superimposed at 1733 cm^{-1} and the xanthone carbonyl stretch occurred at 1667 cm^{-1}. The ^{1}H NMR spectrum showed ester methyl signals at 3.98 and 4.10 ppm as well as six aromatic protons between 7.41 and 8.43 ppm.

The present procedure represents a convenient route to this new xanthone derivative. The analogous 9-oxothioxanthenedicarboxylic acid has been obtained by a multistep sequence involving an S_NAr reaction between 4-nitrophthalimide and thiosalicylic acid.[18] The corresponding acridone derivative has been produced *via* the reaction of diphenyliodonium-2-carboxylate with dimethyl 4-aminophthalate.[19]

4-Methyl- and 4-phenyl-1,2,4-triazoline-3,5-dione (MTAD and PTAD) are potent dienophiles which react rapidly even with unreactive dienes.[20] Reaction of **9** with PTAD in dichloromethane proceeded smoothly at room temperature, the adduct **22a** precipitating as a white solid in near quantitative yield. Similarly, reaction with MTAD gave the product **22b** in quantitative yield. The ^{1}H NMR spectra of the adducts **22a** and **22b** could not be obtained because of their very low solubility in a range of solvents, but the ratio of substrate to dienophile was confirmed as 1 : 1 from elemental analysis. The IR spectrum showed bands at 1770 and 1720 cm^{-1} for the urazole carbonyl moieties and 1667 cm^{-1} for the chromanone carbonyl in **22a**; similar bands were observed for **22b**. The 1-methylxanthone **16a** reacted with MTAD under the usual conditions to yield the adduct **22c** in excellent yield. The presence of the methyl group helped to solubilise the cycloadduct for ^{1}H NMR spectroscopy. The 3-methylxanthone **14a** also gave an excellent yield of the adduct **22d** which ^{1}H NMR spectroscopy showed to be a 1 : 1 mixture of two diastereomers. Crystallisation from ethyl acetate and hexane caused enrichment in one isomer (ratio 2 : 1) although we were unable to achieve complete separation by this or any other means. The two isomers which are epimeric at C-12a result from a lack of diastereofacial control in the cycloaddition, a feature which is characteristic of the behaviour of RTADs with 5-substituted cyclohexa-1,3-dienes.[21] Surprisingly, 5-ethynylcyclohexa-1,3-diene is reported to react stereospecifically with PTAD to give the adduct in which the ethynyl group is *anti* to the triazole ring.[22]

The stereochemistry of each isomer was established by NOE difference spectroscopy. In the minor isomer, the C-15 methyl group resonance appears as a doublet at δ 0.98. Irradiation of this group resulted in enhancement of the bridgehead (C-5)

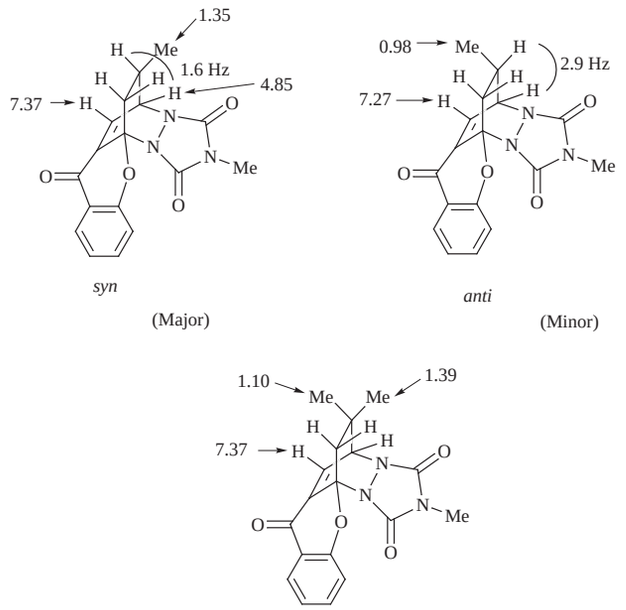


Fig. 1

proton and the alkene (C-6) proton (δ 7.27). The major isomer exhibited a methyl signal at δ 1.35; however irradiation produced no enhancement of the signal due to H-6 (δ 7.37). Thus the major isomer has the C-methyl group *syn* to the triazole ring. Coupling constants between H-15 and the bridgehead H-5 are 2.9 and 1.6 Hz for the minor and major isomers, respectively. Christl[22] noted a coupling constant of 2.6 Hz for a related *anti* ethynyl adduct lending support to our assignments. These assignments (Fig. 1) are also supported by NOESY and NOE difference spectra of the adduct **22e**, an excellent yield of which was obtained from the cycloaddition of the 3,3-dimethyl analogue **14b** with MTAD. Wide melting ranges are observed for many of these compounds, especially **22c**, a feature which has been observed with other RTAD adducts.[23]

Experimental

Reactions requiring anhydrous conditions were performed using oven dried glassware and were conducted under nitrogen. Anhydrous solvents were prepared according to the published procedures[24] and stored over activated 4 Å molecular sieves. Melting points are uncorrected. IR spectra were recorded on a Mattson Galaxy 3000 FT-IR spectrometer. NMR spectra were recorded at 250 MHz on a Bruker WM250 or DPX 250 instrument for $CDCl_3$ solutions; *J* values are given in Hz. Distillations were performed using a bulb-to-bulb (Kügelrohr) apparatus (Büchi GKR-50 glass tube oven) and all boiling points quoted relate to the oven temperature at which distillation commenced. Flash chromatography was performed on silica gel (Sorbsil C60, MPD 60 Å, 40–60 microns) according to the published procedure.[25] The synthesis of the 1-hydroxy-2,3,4,4a-tetrahydro-9*H*-xanthen-9-ones has been described.[9]

9*H*-Xanthen-9-one

A stirred solution of the 1-hydroxytetrahydroxanthone **7** (2.0 g, 9.26 mmol) and toluene-4-sulfonic acid monohydrate (1.0 g, 5.26 mmol) in pyridine (40 cm^3) was heated under reflux for 46 h. The cooled solution was poured into ice–water (150 cm^3) containing conc. HCl (80 cm^3), extracted into chloroform (3 × 70 cm^3) and the combined organic extracts were washed with water (2 × 100 cm^3) followed by aqueous sodium hydroxide (2 M, 2 × 150 cm^3). The dried (Na_2SO_4) organic phases were evaporated to give the *title compound* as a white solid (1.5 g, 83%). Washing with diethyl ether–light petroleum (bp <40 °C), and subsequent recrystallisation from light petroleum (bp 60–80 °C) gave white needles, mp 173–175 °C (lit.,[26] mp 174–176 °C).

1-Acetoxy-1,2,3,4-tetrahydro-9*H*-xanthen-9-one 8a and 3,4-dihydro-9*H*-xanthen-9-one 9

A stirred solution of **7** (1.0 g, 4.63 mmol) and 1,4-diazabicyclo[2.2.2]octane (DABCO) (0.52 g, 4.63 mmol) in glacial acetic acid (30 cm^3) was heated under reflux for 3.5 h. The cooled solution was diluted with water (200 cm^3), and extracted into chloroform (3 × 100 cm^3). The combined organic extracts were washed with 2 M sodium hydroxide (3 × 70 cm^3) and water (2 × 100 cm^3). After drying (Na_2SO_4) the solvent was removed to give a grey oil (1.06 g). The ^1H NMR spectrum of the oil showed the title compounds **8a** and **9** were present in the ratio of 1 : 2.

1-Acetoxy-1,2,3,4-tetrahydro-9*H*-xanthen-9-one 8a

A stirred solution of **7** (1.0 g, 4.63 mmol) and sodium acetate trihydrate (0.63 g, 4.64 mmol) in glacial acetic acid (20 cm^3) was heated under reflux for 4.5 h. After cooling and diluting with water (200 cm^3), the mixture was extracted with chloroform (3 × 70 cm^3). The combined organic extracts were washed with water (2 × 100 cm^3), saturated aqueous sodium hydrogen carbonate (2 × 100 cm^3), and brine (100 cm^3). After drying (Na_2SO_4) removal of the solvent provided a dark oil. Kügelrohr distillation gave a bright yellow oil (0.90 g, 80%), bp 190 °C at 0.04 torr, which crystallised on standing. Recrystallisation from ethyl acetate and hexane gave the title compound **8a** as colourless needles, mp 121–124 °C; ν_{max}(Nujol)/cm^{-1} 1736, 1641 and 1610; δ_H 1.75 (1H, m, H-2), 1.95 (2H, m, H-3), 2.06 (3H, s, Me), 2.16 (1H, m, H-2), 2.71 (2H, m, H-4), 6.20 (1H, t, *J* 3.1, H-1), 7.37 (2H, m, Ar-H), 7.64 (1H, m, Ar-H), 8.18 (1H, dd, *J* 7.9, 1.6, H-8) (Found: C, 69.9; H, 5.5. $C_{15}H_{14}O_4$ requires C, 69.8; H, 5.5%).

1-Hydroxy-1,2,3,4-tetrahydro-9*H*-xanthen-9-one 8b

(a). A solution of the 1-acetoxy compound **8a** (0.20 g, 0.82 mmol) in glacial acetic acid (20 cm^3) containing conc. HCl (3 drops) was kept at room temperature for 2 h with occasional shaking. The mixture was diluted with water (200 cm^3), extracted into ethyl acetate (3 × 70 cm^3) and washed with saturated aqueous ammonium chloride (3 × 70 cm^3) and then with aqueous sodium hydrogen carbonate (3 × 80 cm^3). Evaporation of the dried organic extracts (Na_2SO_4) gave the title compound **8b** as a pale yellow oil (0.16 g, 90%) which readily crystallised. Recrystallisation from ethyl acetate and hexane gave colourless crystals mp 107–108.5 °C (lit.,[10] mp 107–109 °C); ν_{max}(Nujol)/cm^{-1} 3453, 1631 and 1601; δ_H 1.73 to 2.03 (4H, m, H-2, H-3), 2.65 (2H, m, H-4), 3.74 (1H, br s, OH), 5.01 (1H, t, *J* 5.3, H-1), 7.34 (2H, m, Ar-H), 7.60 (1H, m, Ar-H), 8.17 (1H, dd, *J* 7.9, 1.5, H-8) (Found: C, 72.3; H, 5.6. $C_{13}H_{12}O_3$ requires C, 72.2; H, 5.6%).

(b). A stirred solution of 1-ethoxytetrahydroxanthone **8c** (1.67 mmol) in dry dichloromethane (30 cm^3) was treated dropwise at −40 °C with a solution of boron tribromide (2.23 mmol) in dichloromethane (20 cm^3). The resulting orange solution was stirred at below 10 °C until the reaction was complete from TLC inspection. The mixture was poured into ice (50 g) and water (100 cm^3), extracted with dichloromethane (2 × 100 cm^3) and the combined organic extracts were dried (Na_2SO_4). Evaporation provided crude **8b** (75%) which was purified by column chromatography (ethyl acetate–hexane, 1 : 4). The product had physical and spectroscopic properties identical to those described previously.

Preparation of 1-alkoxy-1,2,3,4-tetrahydroxanthen-9-ones

A solution of the diketone **7** (4.63 mmol) and toluene-4-sulfonic acid monohydrate (0.13 g, 0.66 mmol) in methanol, ethanol or ethanol–water (40 cm^3) was heated under reflux until no starting material remained (TLC) (2–170 h). The cooled solution was poured into water (400 cm^3) and extracted with

chloroform (3 × 70 cm^3). The combined organic extracts were washed with aqueous sodium hydroxide (2 M, 2 × 100 cm^3) and brine (100 cm^3). Removal of solvent from the dried organic extracts (Na_2SO_4) gave the crude product which was purified by chromatography or recrystallisation.

The following compounds were obtained by this procedure.

1-Hydroxy-1,2,3,4-tetrahydro-9*H*-xanthen-9-one 8b. From **7** in ethanol–water (4:6) as a yellow-brown oil, chromatography (ethyl acetate–hexane, 1:4) of which gave **8c** (33%) as a pale yellow solid. Continued elution (1:4 to 2:3) gave the title compound **8b** (46%) which had identical physical and spectroscopic characteristics to those described above.

1-Ethoxy-1,2,3,4-tetrahydro-9*H*-xanthen–9-one 8c. From **7** and absolute ethanol as pale brown crystals (70%) after crystallisation from ethyl acetate and light petroleum (bp 60–80 °C), mp 102–103.5 °C; ν_{max}(Nujol)/cm^{-1} 1631, 1607 and 1568; δ_H 1.22 (3H, t, J 7.0, OCH_2CH_3), 1.45 (1H, m, H-2), 1.85 (1H, m, H-3), 2.17 (2H, m, H-3, H-2), 2.65 (2H, m, H-4), 3.74 (2H, q, *J* 7.0, OCH_2CH_3), 4.74 (1H, t, *J* 2.5, H-1), 7.33 (2H, m, Ar-H), 7.59 (1H, m, Ar-H), 8.17 (1H, dd, *J* 7.9, 1.5, H-8) (Found: C, 73.8; H, 6.8. $C_{15}H_{16}O_3$ requires C, 73.8; H, 6.6%).

1-Methoxy-1,2,3,4-tetrahydro-9*H*-xanthen-9-one 8d. From **7** and methanol as colourless crystals (35%) after column chromatography (ethyl acetate–hexane, 3:7) and crystallisation from ethyl acetate and light petroleum (bp 60–80 °C), mp 86.5–88.5 °C; ν_{max}(Nujol)/cm^{-1} 1632, 1609 and 1570; δ_H 1.46 (1H, m, H-3), 1.88 (1H, m, H-3), 2.16 (2H, m, H-2), 2.66 (2H, m, H-4), 3.52 (3H, s, OMe), 4.66 (1H, t, *J* 2.4, H-1), 7.35 (2H, m, Ar-H), 7.61 (1H, m, Ar-H), 8.19 (1H, dd, *J* 7.9, 1.5, H-8) (Found: C, 73.5; H, 6.2. $C_{14}H_{14}O_3$ requires C, 73.0; H, 6.2%).

Acid-catalysed rearrangement of 1-hydroxy-2,3,4,4a-tetrahydro-9*H*-xanthen-9-ones

Method A: toluene-4-sulfonic acid in toluene. A stirred solution of the 1-hydroxytetrahydroxanthone **7** or **13** (4.63 mmol) and toluene-4-sulfonic acid monohydrate (1.47 mmol) in toluene (40 cm^3) was heated under reflux until the reaction was judged complete by TLC. The solvent was removed from the cooled reaction mixture and the residue was dissolved in chloroform (200 cm^3), washed with aqueous sodium hydroxide (1 M, 2 × 100 cm^3) and water (100 cm^3). Evaporation of the dried organic phase (Na_2SO_4) provided the crude product.

Method B: methanesulfonic acid. A solution of the 1-hydroxytetrahydroxanthone **7** or **13** (4.63 mmol) in methanesulfonic acid (30 cm^3) was stirred at room temperature until completion of the transformation. Pouring onto ice (*ca.* 100 g) and water (150 cm^3), extraction into ethyl acetate (2 × 100 cm^3), washing with water (2 × 100 cm^3) and aqueous sodium hydroxide (2 M, 2 × 100 cm^3) and evaporation of the dried organic extract (Na_2SO_4) provided the crude product.

Method C: toluene-4-sulfonic acid in deaerated toluene. A stirred solution of the 1-hydroxytetrahydroxanthone **7** or **13** (4.63 mmol) and toluene-4-sulfonic acid monohydrate (1.47 mmol) in toluene (40 cm^3) at room temperature was deaerated for 15 min using nitrogen. The mixture was heated under reflux under nitrogen until completion of the reaction (TLC). The mixture was allowed to cool to room temperature under the inert atmosphere, diluted with water (200 cm^3) and extracted with ethyl acetate (3 × 70 cm^3). The combined organic extracts were washed with aqueous sodium hydroxide (1 M, 2 × 100 cm^3) and water (100 cm^3) and dried (Na_2SO_4). Evaporation provided the crude product.

The crude products were purified either by recrystallisation or column chromatography.

The following compounds were prepared according to this method.

3,4-Dihydro-9*H*-xanthen-9-one 9. *Method A.*—From xanthone **7** as light brown crystals (95%) after washing the initial light brown semi-solid with light petroleum (bp <40 °C).

Method B.—From **7** as fawn needles (81%) from light petroleum (bp 60–80 °C), mp 109–110 °C; ν_{max}(Nujol)/cm^{-1} 1640 and 1607; δ_H 2.50 (2H, m, H-3), 2.84 (2H, t, *J* 9.2, H-4), 5.84 (1H, dt, *J* 9.6, 4.4, H-2), 6.74 (1H, dt, *J* 9.6, 1.8, H-1), 7.38 (2H, m, ArH), 7.59 (1H, m, Ar-H), 8.22 (1H, dd, *J* 7.9, 1.7, H-8) (Found: C, 78.8; H, 5.1. $C_{13}H_{10}O_2$ requires C, 78.8; H, 5.1%).

3,4-Dihydro-3-methyl-9*H*-xanthen-9-one 14a. *Method B.*—From **13a** as a pale yellow oil (97%) which crystallised on standing, bp 150 °C at 0.04 torr, mp 68.5–70.5 °C; ν_{max}(Nujol)/cm^{-1} 1649, 1631 and 1606; δ_H 1.15 (3H, d, *J* 7.0, Me), 2.59 (1H, dd, *J* 16.1, 9.4, H-4), 2.77 (1H, m, H-3), 2.92 (1H, dd, *J* 16.1, 7.8, H-4), 5.74 (1H, dd, *J* 9.7, 3.7, H-2), 6.07 (1H, dd, *J* 9.6, 1.8, H-1), 7.38 (2H, m, Ar-H), 7.60 (1H, m, Ar-H), 8.22 (1H, dd, *J* 7.9, 1.6, H-8) (Found: C, 79.1; H, 5.7. $C_{14}H_{12}O_2$ requires C, 79.2; H, 5.7%).

3,4-Dihydro-3,3-dimethyl-9*H*-xanthen-9-one 14b. *Method B.*—From **13b** as colourless crystals (94%) from hexane, mp 75–77 °C; ν_{max}(Nujol)/cm^{-1} 1648, 1630 and 1608; δ_H 1.14 (6H, s, 2 × Me), 2.71 (2H, s, H-4), 5.63 (1H, d, *J* 9.5, H-2), 6.64 (1H, d, *J* 9.6, H-1), 7.38 (2H, m, Ar-H), 7.61 (1H, m, ArH), 8.23 (1H, dd, *J* 8.3, 1.6, H-8) (Found: C, 79.8; H, 6.4. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%).

3,4-Dihydro-1-methyl-9*H*-xanthen-9-one 16a and 1-methylidene-1,2,3,4-tetrahydro-9*H*-xanthen-9-one 17a. *Method A.*—The xanthone **15a** provided a yellow-green oil (99%) which crystallised on standing and was shown by ^1H NMR spectroscopy to be a mixture of compounds **16a** and **17a** in a ratio of *ca.* 4:1, from which 3,4-dihydro-1-methyl-9*H*-xanthen-9-one **16a**, mp 84–85 °C, was obtained as pale yellow needles from hexane; ν_{max}(Nujol)/cm^{-1} 1640, 1627 and 1611; δ_H 2.30 (3H, s, Me), 2.32 (2H, m, H-3), 2.78 (2H, m, H-4), 5.55 (1H, m, H-2), 7.35 (2H, m, Ar-H), 7.58 (1H, m, Ar-H), 8.19 (1H, m, H-8) (Found: C, 79.3; H, 5.6. $C_{14}H_{12}O_2$ requires C, 79.2; H, 5.6%).

3,4-Dihydro-1-ethyl-9*H*-xanthen-9-one 16b and (*E*)-1-ethylidene-1,2,3,4-tetrahydro-9*H*-xanthen-9-one 17b. *Method A.*—The diketone **15b** afforded the products **16b** and **17b** as a pale yellow oil (97%) which crystallised on standing.

Method C.—From **15b** as a red oil (100%), crystallisation of which from light petroleum (bp 60–80 °C) gave colourless crystals of (*E*)-1-ethylidene-1,2,3,4-tetrahydro-9*H*-xanthen-9-one **17b**, mp 77.0–78.5 °C; ν_{max}(Nujol)/cm^{-1} 1649, 1630, 1611 and 1590; δ_H 1.84 (3H, d, *J* 1.5, Me), 1.90 (2H, m, H-3), 2.45 (2H, t, *J* 6.2, H-2), 2.79 (2H, t, *J* 6.5, H-4), 7.32 (3H, m, Ar-H, =C*H*Me), 7.59 (1H, m, Ar-H), 8.21 (1H, m, H-8) (Found: C, 79.8; H, 6.3. $C_{15}H_{14}O_2$ requires C, 79.6; H, 6.2%).

1-Butyl-3,4-dihydro-9*H*-xanthen-9-one 16c and (*E*)-1-butylidene-1,2,3,4-tetrahydro-9*H*-xanthen-9-one 17c. *Method A.*—Xanthone **15c** gave a yellow-brown oil which was subjected to column chromatography (ethyl acetate–hexane, 1:9) to provide an inseparable mixture of the title compounds **16c** and **17c** in a ratio of 3:7 as a pale grey oil (99%).

Method B.—Xanthone **15c** provided the title compound **17c** as a yellow oil (76%), bp 170 °C at 0.04 torr; ν_{max}(liquid film)/cm^{-1} 1642 and 1614; δ_H 0.86–3.18 (13H, m, $CH_2CH_2CH_3$, H-2, H-3, H-4), 7.27 (3H, m, =C*H*Pr, Ar-H), 7.52 (1H, m, Ar-H), 8.19 (1H, m, H-8) (Found: C, 80.3; H, 7.2. $C_{17}H_{18}O_2$ requires C, 80.3; H, 7.1%).

1-*sec*-Butyl-3,4-dihydro-9*H*-xanthen-9-one 16d. *Method C.*—From **15d** as a pale yellow oil (92%), bp 175 °C at 0.1 torr; ν_{max}(CCl_4)/cm^{-1} 1646 and 1611; δ_H 0.86 (3H, t, *J* 7.3, CH_2CH_3), 1.06 (3H, d, *J* 6.8, $CHCH_3$), 1.24 (1H, m, CH_2CH_3), 1.54 (1H, m, CH_2CH_3), 2.30 (2H, m, H-3), 2.70 (2H, m, H-4), 3.66 (1H, m, $CHCH_3$), 5.68 (1H, t, *J* 4.5, H-2), 7.35 (2H, m, Ar-H), 7.58 (1H, m, Ar-H), 8.20 (1H, dd, *J* 7.9, 1.6, H-8) (Found: C, 80.0; H, 7.0. $C_{17}H_{18}O_2$ requires C, 80.3; H, 7.1%).

(*E*)-1-(4-Methylbenzylidene)-1,2,3,4-tetrahydro-9*H*-xanthen-9-one 17e. *Method C.*— From **15e** as white florets (100%) from ethyl acetate and hexane, mp 89.5–118 °C; ν_{max}(Nujol)/cm^{-1} 1638 and 1612; δ_H 1.89 (2H, m, H-3), 2.36 (3H, s, Ar-CH_3), 2.70

(2H, m, H-2), 2.85 (2H, t, *J* 6.4, H-4), 7.26 (4H, m, Ar-H), 7.36 (2H, m, Ar-H), 7.61 (1H, m, Ar-H), 8.26 (1H, dd, *J* 8.4, 1.5, H-8), 8.31 (1H, s, =CH-Ar) (Found: C, 83.7; H, 6.0. $C_{21}H_{18}O_2$ requires C, 83.4; H, 6.0%).

4,11a-Ethano-3,3a,4,6,11a,11b-hexahydro-1*H*-furo[3,4-*c*]-xanthene-1,3,6-trione 18a

A stirred solution of 3,4-dihydroxanthone **9** (0.50 g, 2.53 mmol) and maleic anhydride (0.25 g, 2.55 mmol) in toluene (20 cm^3) was heated under reflux for 6 days. After cooling to room temperature, the brown crystalline solid which separated was collected and washed with several portions of toluene. Recrystallisation from ethyl acetate and hexane gave the title compound **18a** (0.27 g, 36%), as pale brown needles, mp 233.5–235 °C; ν_{max}(Nujol)/cm^{-1} 1867, 1840, 1774, 1600 and 1601; δ_H([$^2H_6$]acetone) 1.32 (1H, m, H-4a), 1.64 (1H, m, H-4b), 2.04 (2H, m, H-4a, H-4b), 3.46 (1H, m, H-4), 3.66 (1H, dd, *J* 8.6, 3.1, H-3a), 3.78 (1H, d, *J* 8.6, H-11b), 7.13 (2H, m, Ar-H), 7.38 (1H, d, *J* 6.3, H-5), 7.66 (1H, m, Ar-H), 7.82 (1H, dd, *J* 7.8, 1.7, H-7) (Found: C, 68.6; H, 4.0. $C_{17}H_{12}O_5$ requires C, 68.7; H, 4.1%).

4,11a-Ethano-2,5-dimethyl-1,2,3,3a,4,6,11a,11b-octahydrochromeno[2,3-*e*]isoindole-1,3,6-trione 18b

A stirred solution of the dihydroxanthone **16a** (0.50 g, 2.36 mmol) and *N*-methylmaleimide (0.27 g, 2.43 mmol) in bromobenzene (30 cm^3) was heated under reflux for 4 days. The bromobenzene was removed under reduced pressure and the brown residue was eluted from silica with ethyl acetate–hexane (1:1) to give the title compound **18b** as yellow crystals (0.31 g, 41%) from ethyl acetate and hexane, mp 231–246 °C (decomp.); ν_{max}(Nujol)/cm^{-1} 1775, 1700, 1651 and 1591; δ_H 1.49 (1H, m, H-4a), 1.80 (2H, m, H-4a, H-4b), 2.04 (1H, m, H-4b), 2.47 (3H, s, Me), 2.80 (3H, s, N-Me), 3.06 (1H, dd, *J* 8.6, 3.1, H-4), 3.22 (2H, m, H-3a, H-11b), 7.02 (2H, m, Ar-H), 7.49 (1H, m, ArH), 7.86 (1H, dd, *J* 7.8, 1.7, H-7) (Found: C, 70.3; H, 5.3; N, 4.3. $C_{19}H_{17}NO_4$ requires C, 70.6; H, 5.3; N, 4.3%).

2,4a-Ethano-3,3,4,4-tetracyano-2,3,4,4a-tetrahydro-9*H*-xanthen-9-one 19

Tetracyanoethylene (0.44 g, 2.53 mmol) was dissolved in dry tetrahydrofuran (15 cm^3) and added to 3,4-dihydro-9*H*-xanthen-9-one **9** (0.50 g, 2.53 mmol) in dry tetrahydrofuran (15 cm^3). The mixture was allowed to stand at room temperature for 38 days with occasional shaking. After this period the reaction was complete. Dilution with water (300 cm^3), extraction into chloroform (2 × 100 cm^3) and evaporation of the dried extracts provided a brown oily solid. Trituration with diethyl ether secured the title compound as an olive green solid (0.36 g, 44%), which crystallised from ethyl acetate and hexane as fawn needles, mp 128–138 °C (decomp.); ν_{max}(Nujol)/cm^{-1} 1676 and 1608; δ_H 1.78 (1H, m, H-3b), 1.99 (1H, dt, *J* 13.3, 3.8, H-3a), 2.50 (1H, m, H-3b′), 2.67 (1H, m, H-3a′), 3.92 (1H, m, H-2), 7.24 (2H, m, Ar-H), 7.68 (2H, m, H-1, Ar-H), 8.04 (1H, m, Ar-H) (Found: C, 69.9; H, 3.0; N, 17.2. $C_{19}H_{10}N_4O_2$ requires C, 69.9; H, 3.1; N, 17.2%).

Dimethyl 9-oxo-9*H*-xanthene-3,4-dicarboxylate 21

A stirred solution of 3,4-dihydro-3,3-dimethyl-9*H*-xanthone **14b** (0.50 g, 2.19 mmol), and dimethyl acetylenedicarboxylate (DMAD) (0.3 cm^3, 2.44 mmol) in bromobenzene (20 cm^3) was refluxed for 4 days. The cooled solution was filtered to provide **21** (0.34 g) and concentration of the filtrate and chromatography of the residue (ethyl acetate–hexane, 1:9) gave a further crop (0.13 g) (69%). The ester, mp 174–178 °C, was obtained as colourless crystals from ethyl acetate and hexane; ν_{max}(Nujol)/cm^{-1} 1733, 1667 and 1616; δ_H 3.98 (3H, s, OMe), 4.10 (3H, s, OMe), 7.41 (1H, m, Ar-H), 7.49 (1H, d, *J* 8.4, Ar-H), 7.75 (1H, m, Ar-H), 7.96 (1H, d, *J* 8.4, H-2), 8.30 (1H, dd, *J* 8.0, 1.4, H-8), 8.43 (1H, d, *J* 8.4, H-1) (Found: C, 65.2; H, 3.8. $C_{17}H_{12}O_6$ requires C, 65.4; H, 3.9%).

Preparation of cycloadducts 22

A stirred solution of the 4-substituted-1,2,4-triazoline-3,5-dione (2.36 mmol) in dry dichloromethane (20 cm^3) was treated dropwise with a solution of the dihydroxanthone (2.36 mmol) in dichloromethane (15 cm^3). The initial red colour of the dienophile rapidly dissipated during the addition until a pale pink or colourless solution resulted. Removal of the dichloromethane gave the crude adduct, which was purified by trituration with a hot solvent or by recrystallisation.

The following compounds were prepared by this procedure.

5,12a-Ethano-2-phenyl-2,3,5,12a-tetrahydro-1*H*,7*H*-chromeno[2,3-*c*][1,2,4]triazolo[1,2-*a*]pyridazine-1,3,7-trione 22a. Reaction of the dihydroxanthone **9** with 4-phenyl-1,2,4-triazoline-3,5-dione gave a white precipitate that was collected by filtration. Washing with a small quantity of dichloromethane gave the title compound **22a** as a white powder (65%). Filtration and washing with hot acetone yielded a white powder, mp 179–182 °C; ν_{max}(Nujol)/cm^{-1} 1770, 1720, 1667 and 1606 (Found: C, 67.3; H, 3.9; N, 11.2. $C_{21}H_{15}N_3O_4$ requires C, 67.6; H, 4.1; N, 11.3%).

5,12a-Ethano-2-methyl-2,3,5,12a-tetrahydro-1*H*,7*H*-chromeno[2,3-*c*][1,2,4]triazolo[1,2-*a*]pyridazine-1,3,7-trione 22b. Reaction of 4-methyl-1,2,4-triazoline-3,5-dione (MTAD) with the dihydroxanthone **9** provided a pale pink solution. Removal of solvent gave a gummy solid which was washed with diethyl ether to give the title compound **22b** as a white solid (90%). Trituration with hot ethyl acetate provided a pure sample, mp 210–214 °C (decomp.); ν_{max}(Nujol)/cm^{-1} 1769, 1708, 1640 and 1611 (Found: C, 61.5; H, 3.9; N, 13.3. $C_{16}H_{13}N_3O_4$ requires C, 61.7; H, 4.2; N, 13.5%).

5,12a-Ethano-2,6-dimethyl-2,3,5,12a-tetrahydro-1*H*,7*H*-chromeno[2,3-*c*][1,2,4]triazolo[1,2-*a*]pyridazine-1,3,7-trione 22c. MTAD and the 1-methyldihydroxanthone **16a** provided a white gummy solid on removal of solvent. Washing with diethyl ether gave the title compound **22c** as an off-white solid (76%). Recrystallisation from ethyl acetate and hexane gave colourless prisms; mp 145–165 °C (decomp.); ν_{max}(Nujol)/cm^{-1} 1744, 1711, 1669 and 1607; δ_H 1.72 (1H, m, H-14a), 1.91 (1H, m, H-15a), 2.30 (1H, m, H-14b), 2,51 (1H, m, H-15b), 2.57 (3H, s, Me), 2.87 (3H, s, N-Me), 4.82 (1H, t, *J* 2.8, H-5), 7.15 (2H, m, Ar-H), 7.59 (1H, m, Ar-H), 7.90 (1H, dd, *J* 7.9, 1.6, Ar-H) (Found: C, 62.8; H, 4.7; N, 12.9. $C_{17}H_{15}N_3O_4$ requires C, 62.8; H, 4.7; N, 12.9%).

5,12a-Ethano-2,15-dimethyl-2,3,5,12a-tetrahydro-1*H*,7*H*-chromeno[2,3-*c*][1,2,4]triazolo[1,2-*a*]pyridazine-1,3,7-trione 22d. MTAD and 3,4-dihydro-3-methyl-9*H*-xanthen-9-one **14a** gave an oily residue which was triturated with diethyl ether to yield the title compound **22d** as a white solid (78%). Recrystallisation from ethyl acetate and hexane gave cream needles, mp 158–168 °C (decomp.); ν_{max}(Nujol)/cm^{-1} 1775, 1711, 1674 and 1605; δ_H(*syn*, major isomer) 1.35 (3H, d, *J* 6.2, Me), 2.01–2.15 (2H, br m, H-14), 2.65–2.85 (1H, m, H-15), 2.86 (3H, s, N-Me), 4.85 (1H, dd, *J* 5.7, 1.6, H-5), 7.14 (2H, m, Ar-H), 7.37 (1H, d, *J* 5.7, H-6), 7.63 (1H, m, Ar-H), 7.95 (1H, m, Ar-H) δ_H(*anti*, minor isomer) 0.98 (3H, d, *J* 6.9, Me), 2.01–2.15 (2H, br m, H-14), 2.65–2.85 (1H, m, H-15), 2.85 (3H, s, N-Me), 5.02 (1H, dd, *J* 5.7, 2.9, H-5), 7.14 (2H, m, Ar-H), 7.32 (1H, d, *J* 5.7, H-6), 7.63 (1H, m, Ar-H), 7.95 (1H, m, Ar-H) (Found: C, 62.7; H, 4.6; N, 12.8. $C_{17}H_{15}N_3O_4$ requires C: 62.8; H, 4.7; N, 12.9%).

5,12a-Ethano-2,15,15-trimethyl-2,3,5,12a-tetrahydro-1*H*,7*H*-chromeno[2,3-*c*][1,2,4]triazolo[1,2-*a*]pyridazine-1,3,7-trione 22e. MTAD and 3,4-dihydro-3,3-dimethyl-9*H*-xanthen-9-one **14b** gave the title adduct **22e** as a colourless solid (86%). Recrystallisation from ethyl acetate and hexane gave colourless prisms, mp 149–152 C; ν_{max}(Nujol)/cm^{-1} 1776, 1711, 1676 and 1610; δ_H 1.01 (3H, s, Me), 1.39 (3H, s, Me), 1.67 (1H, d, *J* 12.7, H-14a), 2.27 (1H, d, *J* 12.7, H-14b), 2.86 (3H, s, N-Me), 4.70 (1H, d,

J 5.7, H-5), 7.13 (2H, m, Ar-H), 7.37 (1H, d, *J* 5.7, H-6), 7.62 (1H, m, Ar-H), 7.94 (1H, dd, *J* 7.9, 1.8, Ar-H) (Found: C, 63.7; H, 4.9; N, 12.4. $C_{18}H_{17}N_3O_4$ requires C, 63.7; H, 5.1; N, 12.4%).

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